JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Lanthanoid "Bottlebrush" Clusters: Remarkably Elongated Metal–Oxo Core Structures with Controllable Lengths

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Supporting Information

ABSTRACT: Large metal–oxo clusters consistently assume spherical or regular polyhedral morphologies rather than high-aspect-ratio structures. Access to elongated core structures has now been achieved by the reaction of lanthanoid salts with a tetrazole-functionalized calixarene in the presence of a simple carboxylate co-ligand. The resulting Ln_{19} and Ln_{12} clusters are constructed from apex-fused Ln_5O_6 trigonal bipyramids and are formed consistently under a range of reaction conditions and reagent ratios. Altering the carboxylate co-ligand structure reliably controls the cluster length, giving access to a new class of rod-like clusters of variable length.

Along a size continuum of metal-containing species, situated between mononuclear metal complexes and nanoparticulate materials, there is a region occupied by high-nuclearity coordination clusters that continues to attract and challenge synthetic chemists. These clusters, which we define following Kostakis et al.,[1] provide an opportunity to enter the nanometer size range from the "bottom up", to give a product that is structurally reproducible at the atomic level.[2] As Argent et al. recently pointed out,[2b] while potential applications for these systems are plentiful, the spectacular structures that can be formed often attract just as much attention from a purely aesthetic perspective.[3] Large coordination clusters tend toward symmetrical geometries, forming spherical capsule-like structures,[2b,3a,4] fused polyhedral units,[5] or "molecular wheels".[6] Discrete "rod-like" coordination clusters with multiple repeat units, in contrast, are unknown, to our knowledge.[7] This is intuitively unsurprising, as a tendency to form clusters with a large aspect ratio may incline the system toward the formation of coordination polymers rather than discrete clusters.

Here we describe the synthesis and characterization of some rod-like coordination clusters. The Ln_{19} or Ln_{12} clusters are stabilized by a tetrazole-functionalized calixarene **1** (Figure 1a), which binds along the length of the cluster core, bridging neighboring lanthanoid units. Carboxylate anions cap the assembly, with the length of the cluster core controlled by the choice of carboxylate (acetate or benzoate). The cluster cores are based on apex-fused Ln_5O_6 trigonal bipyramids, which is an unprecedented structure for a coordination cluster.

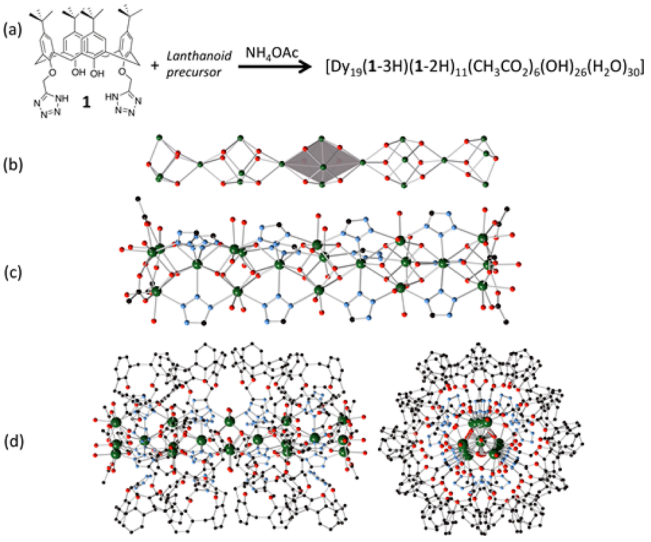

Figure 1. (a) Reaction scheme for the synthesis of the $[Dy_{19}(\mathbf{1}\text{-}3H)(\mathbf{1}\text{-}2H)_{11}(CH_3CO_2)_6(OH)_{26}(H_2O)_{30}]$ cluster, (b) the dysprosium hydroxo core, (c) the primary coordination sphere of the dysprosium cations, emphasizing the tetrazolate–Dy interactions, and (d) the cluster with *tert*-butyl groups and H atoms removed for clarity, side on and end on. Sphere colors: green, Dy; blue, N; red, O; black, C.

The bis-tetrazole calixarene **1** (Figure 1a) was dissolved in ethanol, or 1:1 ethanol:ethyl acetate, along with 1 equiv of the lanthanoid metal salt. The key to producing clusters rather than mononuclear complexes was the use of ammonium acetate to adjust the protonation state of the calixarene, rather than triethylamine as used previously.[8] The ammonium acetate was added as a 1 M aqueous solution, and the resulting solution was allowed to evaporate under ambient conditions, depositing

Received: July 7, 2014
Published: October 4, 2014

crystals after 1−2 weeks. The crystals were of sufficient quality to undertake single-crystal X-ray diffraction studies, although the quality of the data did vary significantly from sample to sample. The quality of the dysprosium-containing systems was consistent under all conditions explored, and these are the focus here.

The results of the structure determinations were consistent with the formation of Dy_{19} clusters with a consistent core structure in three different crystal forms, two monoclinic (**Dy19-A**, **Dy19-B**) and one trigonal (**Dy19-C**). While there are some subtle variations in the co-ligand distribution in these clusters, leading to variations in the crystal packing (see SI), the key features are common to all, so only **Dy19-B** is discussed in detail. The neutral cluster found in **Dy19-B** is best formulated as $[Dy_{19}(\mathbf{1}\text{-}3H)(\mathbf{1}\text{-}2H)_{11}(CH_3CO_2)_6(OH)_{26}(H_2O)_{30}]$, while noting that the location of the protons in such a structure is subject to some uncertainty. Considering the core of the cluster first, the metal atoms form a sequence of apex-sharing trigonal bipyramids with 2-fold rotational symmetry perpendicular to the long axis of the core and *quasi*-3-fold symmetry along the long axis (Figure 1b). The cluster is terminated at each end with a μ_3-O atom replacing the apical metal atom and *syn-syn* acetate anions bridging the terminal metal atom triangles. The metal equatorial triangles are close to parallel (deviation of <1°) but are rotated (Figure 1d); relative to the central metal triangle, the penultimate triangles deviate by ∼12° and the terminal triangles by ∼20°. Each triangular face of the trigonal bipyramids is capped with a μ_3-O atom. This cluster is only the second example of trigonal bipyramidal geometry in a lanthanoid cluster, the first being a single bipyramid supported by carboxylate ligands.[9] It is notable that the trigonal bipyramid units are each bridged by three $\mu_{1,2,3}$-tetrazolate moieties, as shown in Figure 1c. While tetrazole ligands are well known as bridging ligands in coordination polymers,[10] their presence as bridging ligands in discrete clusters is rare, and those known are cyclic clusters.[11,12] The remainder of the lanthanoid coordination spheres comprises terminal hydroxo O atoms. The equatorial Ln atoms are 8-coordinate (N_2O_6, or for the terminal Ln atoms, NO_7) with a geometry best described as a distorted square antiprism, and the apical Ln atoms are 9-coordinate (N_3O_6, distorted tricapped trigonal prism).

It seems likely that the calixarene ligand **1** is key to the stabilization of this metal cluster. The cluster contains 12 calixarene molecules along the length of the cluster, giving the "bottlebrush" appearance to the cluster (Figure 1d). In all cases, the calixarene is coordinated to the primary coordination sphere through one of the two tetrazolate moieties. The other interacts with the second coordination sphere of the metal,[13] presumably strengthening the interaction of the ligand with the metal−hydroxo cluster.

These results demonstrate that the synthesis of this unusual Ln_{19} cluster is reproducible and, based on unit cell determinations at least (see SI), applicable to many of the heavier lanthanoid elements from Eu to Lu. To date, no clusters could be crystallized with the lighter lanthanoid elements (La−Nd).

An attractive feature of these clusters is the distinction between the ligands (calixarene **1**) bound to the side faces of the rod-like cluster and the capping ligands (acetate anions). This suggested there might be potential to change the length of the cluster by altering the ratio of the two ligands. This method is well established for controlling crystal morphology, where an additive selective for the fast growing face of a needle-like crystal is introduced to reduce the aspect ratio.[14] Increasing the relative amount of acetate did not cause a smaller cluster to be isolated, although the packing of the cluster in the crystal was altered (see SI, **Dy19-C**). Varying the metal to calixarene ratio as 2:1, 1:1, 1:2, and 1:3 did not cause a change in the cluster deposited. Finally, substituting acetate with benzoate did cause a change in the cluster, with a smaller Ln_{12} cluster isolated. Crystals again formed readily from 1:1 ethanol:ethyl acetate solutions. The structure determination of the dysprosium complex **Dy-12** gave results consistent with a cluster formulated as $[Dy_{12}(\mathbf{1}\text{-}3H)_3(\mathbf{1}\text{-}2H)_3(PhCO_2)_5(OH)_{16}(H_2O)_{21}]$. Remarkably, the core of the cluster is constructed from the same trigonal bipyramidal motif but is shorter. One end is terminated with an apical Dy atom, with the associated trigonal bipyramidal edges bound to disordered benzoate anions and water molecules, rather than tetrazole moieties (Figure 2). This may explain why altering the carboxylate:calixarene ratio does not affect the cluster length isolated; the selectivity of the ligands between the capping positions and sides of the cluster may not be as high as the Ln_{19} structures suggested. The other end of the cluster is essentially the same as found in the acetate systems. Based on unit cell determinations, isomorphous Ln_{12} clusters have been isolated for lanthanoids ranging from Tb to Yb (see SI). The driving force for the change in isolated cluster may be the relative solubilities and charges of the components of the mixture of clusters formed in solution. Exploration of the impact of a range of carboxylates is underway.

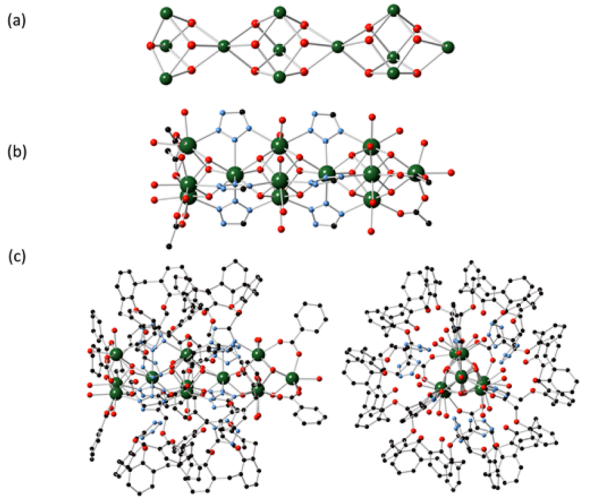

Figure 2. Simplified representations of the cluster $[Dy_{12}(\mathbf{1}\text{-}3H)_3(\mathbf{1}\text{-}2H)_3(PhCO_2)_5(OH)_{16}(H_2O)_{21}]$: (a) the Dy_{12} dysprosium hydroxo core, (b) the primary coordination sphere of the dysprosium cations, emphasizing the tetrazolate−Dy interactions, and (c) the cluster with *tert*-butyl groups and H atoms removed for clarity, side-on and end-on.

Magnetic studies of the **Dy19-B** cluster found that the room-temperature value of $\chi_M T$, 270.6 cm^3 K mol^{-1}, is similar to the expected value of 268.4 cm^3 K mol^{-1} for 19 uncoupled Dy^{III} ions ($S = {}^5/_2$, $L = 5$, ${}^6H_{15/2}$ $g_J = 4/3$). As the temperature is lowered, $\chi_M T$ decreases slightly from the room temperature value, to 261.5 cm^3 K mol^{-1} at 100 K (Figure 3a), this is likely to be from the progressive depopulation of the excited Stark sublevels.[15] $\chi_M T$ then sharply decreases to a minimum value of 242.2 cm^3 K mol^{-1} at 13 K. As the temperature is decreased further, $\chi_M T$ increases rapidly to 301.1 cm^3 K mol^{-1} at 2 K,

dx.doi.org/10.1021/ja506677h | J. Am. Chem. Soc. 2014, 136, 15122−15125

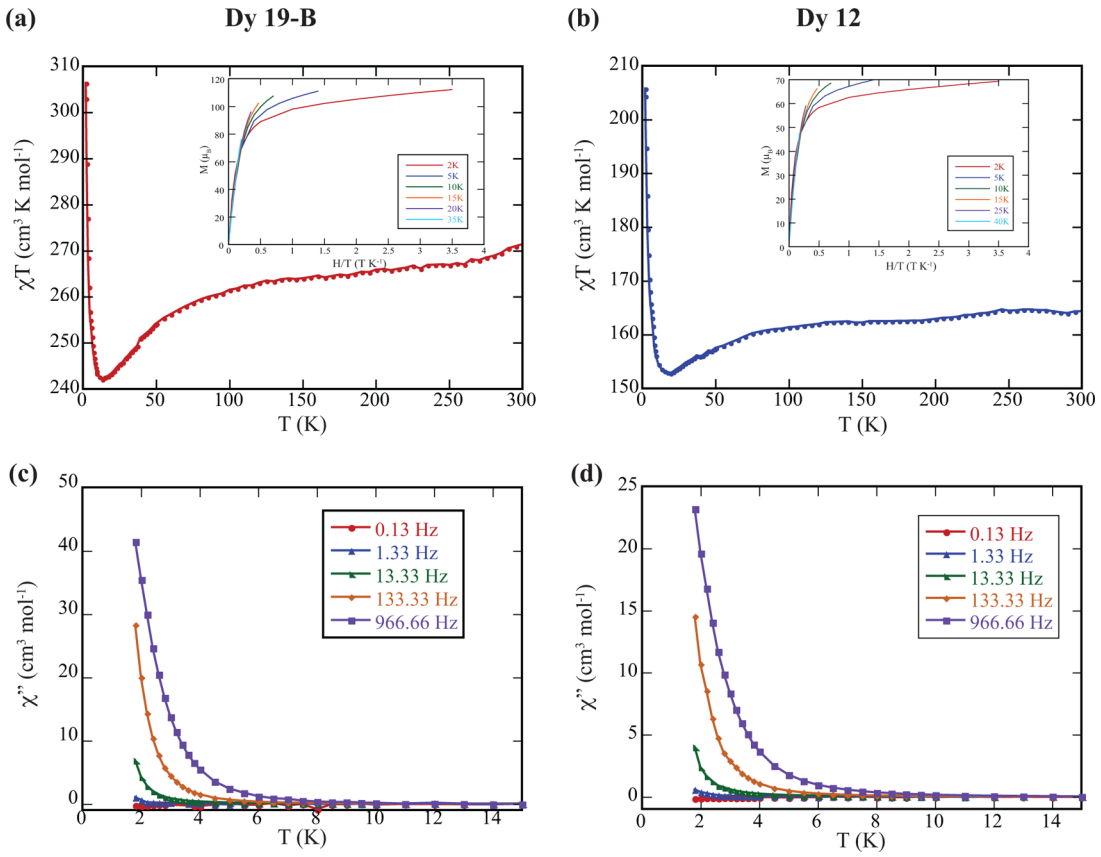

Figure 3. Temperature dependence of the $\chi_M T$ product for the (a) **Dy19-B** and (b) **Dy12** clusters in a 100 Oe applied field. Inset: M vs H/T plots at different temperatures below 50 K. The frequency dependence of the out-of-phase ac susceptibility (χ'') vs T for the **Dy19-B** (c) and **Dy12** (d) clusters.

suggestive of significant ferromagnetic interactions between the metal centers.[16] The field-dependent magnetization (Figure 3a, inset) is not superimposable below 35 K and rises rapidly in low field. At higher fields, the linear variation leads to a non-saturating value of 110.2 μ_B (19 × 5.80 μ_B), which is similar to values reported for other Dy^{III} complexes and is likely the result of significant anisotropy and the possible occurrence of low-lying states.[16,17] The **Dy12** cluster gave similar results (Figure 3b). The room-temperature value of $\chi_M T$, 164.1 cm^3 K mol^{-1}, is similar to the expected value of 169.5 cm^3 K mol^{-1} for 12 uncoupled Dy^{III} ions. Like the **Dy19-B** complex, the M vs H/T plots (Figure 3b, inset) obtained for the **Dy12** complex are non-superimposable, and at higher fields, the linear variation of M vs H/T results in a non-saturating value of 69.3 μ_B (~12 × 5.80 μ_B).

Variable ac SQUID measurements were performed on the **Dy19-B** (Figure 3c) and **Dy12** (Figure 3d) complexes from 1.8 to 15 K and a range of frequencies between 0.13 and 966.66 Hz with a 2 Oe oscillating field. **Dy19-B** and **Dy12** complexes have a significant out-of-phase (χ'') signal below 8 K. (The in-phase component of the susceptibility, χ', is shown in Figure S6.) Although there is no maximum in χ'', the frequency dependence of the signal is consistent with single-molecule magnet (SMM) behavior with low blocking temperatures. As a result of the low blocking temperature (T_B < 1.8 K) of the complexes, no hysteretic behavior was observed in the magnetization curves at or above 1.8 K. The poor performance of these compounds as SMMs is consistent with previous work that shows that lanthanoid complexes with large numbers of metal ions generally have lower blocking temperatures than complexes with fewer metal atoms.[18]

Solution-phase light-scattering measurements of the reaction mixtures indicated an increase in the average particle size in solution upon the addition of increasing amounts of ammonium acetate (Figures S7–S10, Tables S1, S2). This is consistent with the formation of clusters, although these could be of various sizes, as often occurs in lanthanoid cluster chemistry.[2a] Subsequent addition of triethylamine resulted in a *decrease* in average particle size (Figure S10b), suggesting that the increases observed were not the result of simple hydrolysis of the lanthanoid salt but were reversible, with the triethylamine presumably driving the formation of the mononuclear calixarene complex.[8] Size increases were also observed upon addition of ammonium benzoate (Figures S11, S12, Table S3), but to a lower maximum size than found with acetate, consistent with the solid-state results.

Discrete rod-like metal clusters are rare, and to the best of our knowledge there are no examples reported to date that achieve an aspect ratio close to that of the system reported here (~7:1, based on metal atom distances).[6] Calixarenes are well known to support metal coordination clusters, forming the more common spherical or polyhedral clusters.[3a,5a,b,19] Similarly, while "clusters of clusters" are known for lanthanoid oxo systems,[20] these are cyclic, such as tetrameric and pentameric cycles of cubanes.[21] This work demonstrates that an appropriate combination of ligands allows for formation of rod-like metal clusters. It was found that straightforward alteration of ligand components allows synthesis of structurally

dx.doi.org/10.1021/ja506677h | J. Am. Chem. Soc. 2014, 136, 15122–15125

similar metal clusters of varying lengths. Access to this family of clusters will allow evaluation of cluster properties as a function of size and shape.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, single-crystal X-ray structures, magnetic measurements, light-scattering data, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.D. gratefully acknowledges The Australian Institute of Nuclear Scientists and Engineers (AINSE) Ltd for provision of a post-graduate research award (AINSE PGRA 2012). We acknowledge use of the facilities and scientific and technical assistance of the Australian Microscopy and Microanalysis Research Facility at the Centre for Microscopy, Characterisation, and Analysis, The University of Western Australia, a facility funded by the University, State and Commonwealth Governments.

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(6) Our working definition of "rod-like" is a system with multiple repeat units. It is important to note, however, reports of Ln_{14} clusters comprising of a Ln_6 octahedron fused at opposite apexes with square pyramids, and Ln_9 clusters with two square pyramids fused at the apexes. (a) King, P.; Stamatatos, T. C.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7379. (b) Hoshino, N.; Ako, A. M.; Powell, A. K.; Oshio, H. *Inorg. Chem.* **2009**, *48*, 3396. (c) Cheng, C.-Y.; Stamatatos, T. C.; Christou, G.; Bowers, C. R. *J. Am. Chem. Soc.* **2010**, *132*, 5387. (d) Miao, Y. L.; Liu, J. L.; Leng, J. D.; Lin, Z. J.; Tong, M. L. *CrystEngComm* **2011**, *13*, 3345.

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